Exergy: the quality of energy
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1 Introduction

Characteristic for our society is a massive consumption of goods and energy. Continuation of this way of life in the long term is only possible if the use of raw materials and fuel will be reduced considerable. This will require that goods and useful energy are produced in a more sustainable way. Waste of raw material and energy should be avoided and losses during conversion and transport need to be reduced as far as possible. The aim for a sustainable production of goods and ready for use energy is a great challenge of our future society.

For this ambition thermodynamics (= the science of energy conversion) will show the direction we have to go. In case of energy conversion this is obvious. The purpose of such systems is the conversion of energy from one form into the other. In case of chemical processes this seems to be less obvious. Since the properties of matter are completely determined by their energetic conditions, thermodynamics will provide the basis for the analysis and optimisation of the chemical conversion of matter. Through applying thermodynamics for energy conversion systems as well as chemical processes the minimal required amount of energy can be determined. Moreover thermodynamics are useful to show where losses do occur and to determine their magnitude. To make clear how the quantity "exergy" can be used for this purpose mainly examples that are concerned with energy conversion are shown. The same considerations however are applicable to chemical processes.

Why the introduction of an additional quantity "exergy" and what is the meaning of this quantity? In practice thermodynamics are often used to determine the performance of processes and plants. In case of chemical processes this implies determining the required amount of raw material and energy per unit product; in case of energy conversion plants determining conversion efficiencies is the central issue. Determining the performance in these cases can be easily done without using the quantity exergy. However the application of the quantity exergy will be useful if differences in performance between alternative plants have to be explained or if plants have to be optimised. To illustrate this table 1 shows characteristic thermal efficiencies for a few conversion options, assuming natural gas as the primary fuel.

Table 1 Thermal efficiencies for a few conversion options

plant	efficiency
electrical power plant	55 %
central heating boiler	95 %
combined heat and power (CHP) plant	80 %

It appears that power production with an electrical power plant leads to much lower conversion efficiencies than the production of hot water in a central heating boiler. Also in case of combined production of heat and power in so-called CHP plants higher conversion efficiencies can be achieved. These efficiencies are determined by using only amounts of energy. However the second law of thermodynamics learns that energy is not only characterised by its amount but also by its quality. This quality is very important in case of energy conversion as loss of quality can occur during conversions without immediate loss of energy to the environment. In thermodynamics the property "entropy" has been introduced to

enable quantifying losses in quality. Entropy however is not a direct measure for the quality of energy, while such a direct measure is very useful for assessing and optimising energy conversion systems. The quality of energy can be indicated in a for engineers comprehensible way as "the potential to convert energy into work": this is the amount of work that can be obtained from an amount of energy under ideal conversion conditions (using reversible processes). This potential to produce work is called "exergy". The quantity exergy originates from the application of thermodynamics on energy conversion systems and must not be seen as a quantity of classical thermodynamics. The importance of this quantity will become clear during analysing and optimising energy systems as well as chemical processes.

The quantity exergy is based of course on thermodynamic concepts. To determine exergy values as well as to explain differences in exergy values and exergy losses basic knowledge of thermodynamics is indispensable. Before focusing on the quantity exergy the necessary thermodynamic concepts will be discussed first.

2 Thermodynamic concepts

2.1 Main laws of thermodynamics

Thermodynamics are based on experience, experience with nature that shows which conversions from one kind of energy into the other are possible and which are not. In the following several kinds of energy will play a role like: kinetic energy, potential energy, internal energy, heat, work, electrical energy and chemical energy. The most well known statements about these conversions, based on experience with nature, are defined as the first and second law of thermodynamics.
The first law of thermodynamics says:

> **"energy can't be lost, neither it can be obtained from nothingness"**

This law indicates that for an arbitrary system the difference between the amount of energy that is transferred into the system and the amount that is transferred from the system should equal the amount that is accumulated in the system during the process. This law makes it possible to draw up energy balances for any arbitrary system.

This first law, also indicated as the conservation of energy principle, shows in fact the similarity between the different kinds of energy. However this law cannot be applied without considering other phenomena during energy conversion. Different kinds of energy not only exhibit similarities but also differences; not every energy conversion is possible if the first law of thermodynamics is satisfied. Nature shows that specific kinds of energy can be converted in every other kind of energy, but there are also kinds of energy for which this is not true. This experience is defined in the second law of thermodynamics. Carnot has formulated this characteristic of nature in the middle of the nineteenth century as follows:

> **"Work can always be converted completely into heat, but heat cannot always be converted entirely into work"**

Also Clausius, Thomson and Planck have formulated this characteristic of nature each in his own words. Actually the meaning of all these formulations is the same. They can be summarised as follows:

"Work is a kind of energy that can be converted completely into heat by any arbitrarily process; however it is impossible to design a process that is able to convert the produced heat completely into work in order to restore the initial state entirely"

The second law of thermodynamics shows that work can be converted completely in any other kind of energy but that this is not the case with heat. In our strongly mechanised society, that consumes work on a large scale, work is more valuable than heat. Therefore based on the second law of thermodynamics the value of an amount of energy is supposed to equal the maximum amount of work that can be obtained from this amount of energy.

The meaning of these thermodynamic laws can be illustrated by considering an arbitrarily closed system for de production of work as shown in figure 1. Within this system a power cycle takes place that receives an amount of heat Q_1 from a hot reservoir at temperature T_1 and discharges an amount of heat Q_2 to a cold reservoir at temperature T_1. It is assumed that the temperature at which heat is transferred into or from the system is the same as the temperature of the corresponding reservoir. In case of a reversible power cycle the produced power is called W_{rev}. The efficiency of the reversible process is defined as:

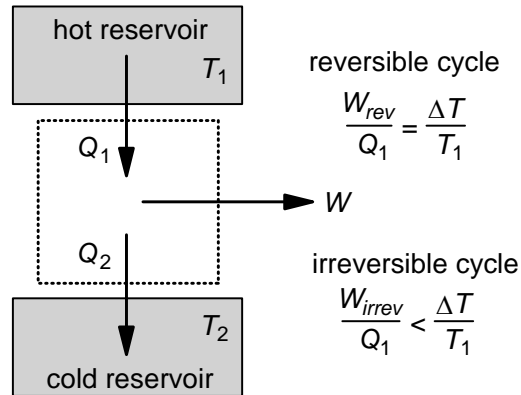$$\eta = \frac{W_{rev}}{Q_1} \tag{1}$$

Figure 1 *Application of the second law of thermodynamics on a closed power cycle*

It is proved that the efficiency of such a reversible power cycle depends only on the temperature of both heat reservoirs. This result has resulted in the definition of the thermodynamic temperature scale. This temperature scale has been chosen such that the efficiency of a reversible power cycle equals the ratio between de temperature difference ($\Delta T = T_1 + T_2$) of the reservoirs and the temperature T_1 at which heat is transferred into the power cycle:

$$\eta = \frac{W_{rev}}{Q_1} = \frac{\Delta T}{T_1} \tag{2}$$

Using the thermodynamic temperature scale the amount of work from a reversible power cycle can be determined with:

$$W_{rev} = (1 - \frac{T_2}{T_1}) \cdot Q_1 \tag{3}$$

The term $(1 - T_2/T_1)$ is often called the Carnot-efficiency. Carnot has derived this equation assuming a reversible cycle containing an ideal gas and applying the ideal gas temperature scale. Today this equation is defined by the choice of the thermodynamic temperature scale. The term $(1 - T_2/T_1)$ indicates the maximum amount of work that can be obtained from the amount of heat Q_1 transferred into the system while using a cold reservoir at temperature T_2.

2.2 The properties enthalpy and entropy

Thermodynamic properties are used to define the thermodynamic state of a system. A short discussion of the properties enthalpy and entropy is presented here as these properties are in particular important to determine the exergy of an amount of matter.

The quantity enthalpy of an arbitrary amount of substance is defined as:
$$H = U + p \cdot V \tag{4}$$
The enthalpy of an amount of substance can be written thus as the sum of the internal energy and the product of pressure and volume of the substance. Differentiating these equation gives:
$$dH = dU + p \cdot dV + V \cdot dp \tag{5}$$
By applying the first law on a compressible substance in a closed system undergoing a reversible process equation (6) can be derived. This equation says that the amount of heat, supplied as a consequence of an infinitesimal change of state, equals the sum of the change of internal energy of the substance and the product of pressure and the change in volume:
$$dQ = dU + p \cdot dV \tag{6}$$
From the equations (5) and (6) it results that the relation between the change in enthalpy and the supplied heat to the substance is:
$$dQ = dH - V \cdot dp \tag{7}$$
It appears that as long as the pressure of the substance is constant, the change in enthalpy equals the amount of heat supplied to the substance.

Another property, closely related to the supplied heat, is the quantity entropy. To clarify the meaning of this property the system shown in figure 1 will be used.
In thermodynamics it postulated that heat is positive as it is transferred into the considered system. Furthermore it is assumed that work has a positive sign as it is produced by the system and delivered to the environment. As a consequence of the first law of thermodynamics it must be that:
$$W_{rev} = Q_1 + Q_2 \tag{8}$$
In this case the value of Q_2 will be negative.
By rewriting equation (1.2) it appears that:
$$\frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{9}$$
This equation can be reorganised resulting in:
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{10}$$
Up to now it is assumed that the system in figure 1 undergoes a reversible power cycle. The amount of work that can be obtained with an irreversible power cycle from the same amount of heat Q_1 will always less than with the reversible process, thus:
$$\frac{W_{rev}}{Q_1} < \frac{\Delta T}{T_1} \tag{11}$$

In a similar way as has been done for the reversible case for the irreversible it can be derived that:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0 \tag{12}$$

To obtain one general applicable equation, for reversible as well as irreversible processes, the equations (10) and (12) can be combined into the equation:

$$\sum \frac{Q}{T} \le 0 \tag{13}$$

In case of systems undergoing a cycle that transfers heat at changing temperature levels one can prove that the following equation applies:

$$\oint \frac{dQ}{T} \le 0 \tag{14}$$

Suppose that a closed system undergoes a process that brings the system in a reversible way from condition 1 to condition 2 and after that in a different but also reversible way from condition 2 to condition 1. The closed system then undergoes a reversible cycle, for which the following equation is valid:

$$\int_{1\,(rev)}^{2} \frac{dQ}{T} + \int_{2\,(rev)}^{1} \frac{dQ}{T} = 0 \tag{15}$$

This equation is valid for any other reversible way through which the closed system goes from condition 1 to condition 2. From this it may be concluded that $\int_{1}^{2} dQ/T$ during a reversible transition from condition 1 to condition 2 always will have the same value. This means that the system has a property for which the change in value during transition from condition 1 to condition 2 is determined by summing up dQ/T over the covered way. This property is called the entropy and is represented by the symbol S:

$$S_2 - S_1 = \int_{1}^{2} \frac{dQ}{T} \qquad \text{or} \qquad dS = \frac{dQ}{T} \tag{16}$$

2.3 The meaning of Δs_{irrev}

Suppose that the closed system undergoes a cycle where the transition from condition 1 to condition 2 is irreversible while the transition from condition 2 to condition 1 is reversible. As the total cycle is irreversible it applies that:

$$\int_{1\,(irrev)}^{2} \frac{dQ}{T} + \int_{2\,(rev)}^{1} \frac{dQ}{T} < 0 \tag{17}$$

Since the transition from condition 1 to 2 is supposed to be reversible from equation (16) it follows:

$$\int_{2\,(rev)}^{1} \frac{dQ}{T} = S_1 - S_2 \tag{18}$$

As a consequence of equations (17) and (18) it results:

$$\int_{1\,(irrev)}^{2} \frac{dQ}{T} < S_2 - S_1 \tag{19}$$

For this equation can also be written:

$$S_2 - S_1 = \int_{1\,(irrev)}^{2} \frac{dQ}{T} + C \tag{20}$$

In this equation C must be positive. The size of C depends on the extent of the irreversibility's during transition from condition 1 to condition 2. In case of a highly irreversible transition C will have a high value; the value of C will be low in case of a little irreversible transition. The value of C will become 0 only in case of a reversible transition. Therefore C can be seen as a contribution of the irreversibility's to the entropy increase and is called the irreversible entropy increase (or entropy production) indicated as ΔS_{irrev}. So, from the second law it appears that any closed system can be characterised by the property "entropy"; the change of this property during a transition from condition 1 to condition 2 will result from the following equation:

$$S_2 - S_1 = \int_{1}^{2} \frac{dQ}{T} + \Delta S_{irrev} \tag{21}$$

On a differential basis this equation takes the form:

$$dS = \frac{dQ}{T} + dS_{irrev} \tag{22}$$

To derive this equation it is assumed that the heat flow dQ is positive if this flow is transferred into the system. The temperature T in this equation is the temperature of the heat flow at the system border. By applying these equations these assumptions have to be considered carefully.

3 Exergy

3.1 Definition of the quantity exergy

In the introduction the quantity exergy is indicated as "the potential to convert energy into work". Obviously the meaning of this quantity is limited to kinds of energy for which the potential to produce work does not equal the energy content, that is kinds of energy that can not be converted fully into work. From the kinds of energy mentioned in section 2.1 the kinetic energy, potential energy and electrical energy can be converted completely into work by applying reversible conversion systems. This means that the exergy of these kinds of energy is the same as the energy content. So the quantity exergy is mainly important for heat, internal energy and chemical energy.
Heat, work and flows of matter have to be considered for the analysis of chemical plants and energy conversion plants. An exergy analysis of these types of plants will require exergy values for heat and flows of matter. In this chapter equations will be derived that can be used to determine these exergy values.

In general it may be expected that a thermodynamic system, which is not in equilibrium with its environment, has the potential to produce work. In this respect an amount of matter can be seen as a thermodynamic system. When such a system is brought into equilibrium with the environment it will be able to produce work and thus the potential of the system to produce work will be reduced. The maximum amount of work will be derived when the system is brought into equilibrium with the environment in a reversible way. This maximum amount of work is defined as the exergy of the system. As a consequence of this definition it is obvious that the exergy of a system is zero when it is fully in equilibrium with the environment.

3.2 The exergy of heat

In section 2.1 it is concluded that an amount of heat, derived from a hot reservoir at temperature T_1, can only partly be converted into work. The remainder is transferred to a heat reservoir at a lower temperature. The produced work is maximally in case of a reversible cycle. Suppose that an amount of heat dQ, at temperature T, is supplied to a reversible power cycle that uses the environment, at temperature T_0, as the cold reservoir. The work obtained from this cycle becomes:

$$dW_{rev} = (1 - \frac{T_0}{T}) \cdot dQ \tag{23}$$

The remaining heat is transferred to the environment at temperature T_0. This heat cannot exchange energy with the environment any longer and is therefore supposed to be in (thermal) equilibrium with the environment. This means that the amount of work dW_{rev} produced by the cycle is the exergy dEx of the quantity of heat dQ.

In practise heat is usually extracted from fluid flows that are cooled down during heat transfer. Extracting heat then occurs under continuously changing temperature conditions. When during a heat transfer process the condition of the heat source changes from condition 1 to condition 2, the exergy of the heat derived from the heat source becomes:

$$Ex_Q = \int_1^2 dEx_Q = \int_1^2 (1 - \frac{T_0}{T}) \cdot dQ \tag{24}$$

This equation can be used generally to determine the exergy of an amount of heat.

3.3 The exergy of an amount of matter

The exergy of an amount of matter is defined by the amount of work that will be obtained from a system that brings the matter into equilibrium with the environment by reversible processes. To determine the amount of work unambiguously the system for the conversion of the matter must be defined more accurately. It is agreed that such a system should have the following characteristics:
a) Only reversible processes take place in the system
b) The system is open, has a constant volume and a steady flow is entering and leaving the system
c) The kinetic and potential energy of the matter is not taken into consideration (is assumed to remain unchanged)
d) Heat can be transferred only from or to the environment (at temperature T_0)
e) For the conversion of matter into environmental components only matter from the environment (at environmental conditions) should be used
f) At the outlet of the system matter is entirely in equilibrium with the environment
The exergy of an amount of matter is defined as the net amount of work that is obtained when the amount of matter has passed such a system.

First the exergy of an amount of matter will be determined without considering changes in the chemical composition of this matter. As will be explained later the exergy derived in this way is also called the thermo-mechanical exergy.
Figure 2 shows a system that brings an amount of matter in (thermo-mechanical) equilibrium with the environment. This means that the matter leaves the system at environmental temperature and pressure.
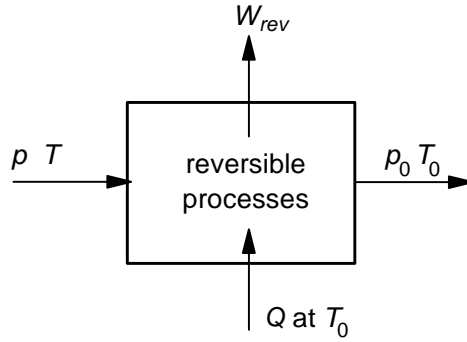
Figure 2 *System with reversible processes that brings an amount of matter into equilibrium with the environment*

Applying the first law on the system shown in figure 2 and neglecting the changes in kinetic and potential energy of the matter at inlet and outlet of the system it becomes:

$$Q = (H_0 - H) + W_{rev} \tag{25}$$

Using equation (1.22) for an reversible process gives:

$$dQ = T \cdot dS$$

As the system can only exchange heat with the environment for this heat can be written:

$$Q = T_0 \cdot (S_0 - S) \tag{26}$$

An equation for work produced by the system can be obtained by combining equations (25) and (26):

$$W_{rev} = (H - H_0) - T_0 \cdot (S - S_0) \tag{27}$$

This represents the work obtained when the amount of matter is brought into equilibrium by applying a system as defined for determining the exergy of matter. Thus the exergy of an amount of matter can be determined with equation (27):

$$Ex = (H - H_0) - T_0 \cdot (S - S_0) \tag{28}$$

At the right side of this equation only properties of state are used. Some of these properties are depending on the condition of the environment. Only after defining the environment unambiguously the quantity exergy can also be seen as a property.

Equation (28) can be used to determine the exergy of an amount of matter. In case of a fluid flow an amount of matter is passing per unit of time. The exergy of a fluid flow then becomes:

$$Ex_{flow} = \Phi_m \cdot (h - h_0) - T_0 \cdot (s - s_0) \tag{29}$$

3.4 Exergy losses

The driving forces applied in the considered processes determine the magnitude of exergy losses. On the other hand driving forces are determining equipment size and the time processes need to develop. Therefore exergy losses have to be weighted against equipment size and capital costs. Finally operational costs and other relevant performance factors, like e.g. emissions, have to be balanced against capital costs. During design and optimisation of plants, the determination of exergy losses will be very useful, because they show how much exergy, or potential to produce work, will be lost in a specific unit of the plant. At normal operation many processes in large plants can be considered to take place in open, steady flow systems as e.g. in heat exchangers, compressors, turbines, furnaces or reactors. To derive a general equation for the exergy loss of such processes figure 3 will be used. It is assumed that

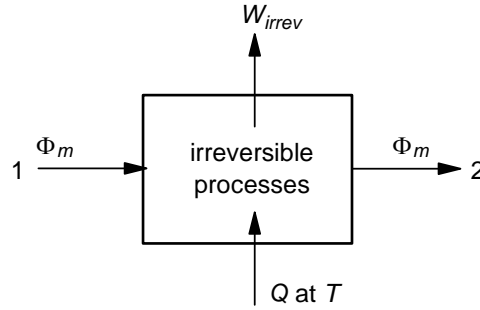the same amount of matter that enters the system will also leave the system during a considered period of time.

Figure 3 *Open system with steady flow*

The exergy loss in the system due to the irreversible processes can be determined by using the exergy balance of the system:

$$Ex_{loss} = Ex_{in} - Ex_{out} \tag{30}$$

The exergy loss of the system in figure 3 can be determined with this equation if the exergy flows entering and leaving the system are known. Exergy is entering the system with mass flow 1, with exergy Ex_1, and a heat flow at temperature T. Exergy leaves the system with mass flow 2, with exergy Ex_2, and the flow of work W_{irrev}. Equation (30) can then be written as:

$$Ex_{loss} = Ex_1 + \int_1^2 (1 - \frac{T_0}{T}) \cdot dQ - Ex_2 - W_{irrev} \tag{31}$$

The exergy change of the flow of matter passing the system can be calculated using equation (29):

$$Ex_1 - Ex_2 = (H_1 - H_2) - T_0 \cdot (S_1 - S_2) \tag{32}$$

As it may be assumed that changes in potential energy and kinetic energy can be neglected, the energy balance of the system in figure 3 can be written as:

$$H_2 - H_1 + W_{irrev} - Q = 0 \tag{33}$$

Combining equations (31), (32) and (33) will deliver the following equation for the exergy loss of the system:

$$Ex_{loss} = T_0 \cdot \left((S_2 - S_1) - \int_1^2 \frac{dQ}{T} \right) \tag{34}$$

The system in figure 3 converts an amount of matter at state 1 in an amount of matter at state 2. De entropy change due to this conversion can be determined by applying equation (21). Combining this equation with equation (34) gives:

$$Ex_{loss} = T_0 \cdot \Delta S_{irrev} \tag{35}$$

From this equation it appears that the exergy loss in a open system with steady flow equals the product of ambient temperature and the irreversible entropy increase (also called "entropy production") of the flow of matter through the system. Equation (35) is, in a somewhat different form, also called the Gouy-Stodola-equation.

2.4 Dividing exergy in thermo-mechanical and chemical exergy

The exergy of an amount of matter is determined by using a system that brings the matter in equilibrium with the environment. Full equilibrium with the environment is achieved when

the temperature of the considered amount of matter is the same as the temperature of the environment and the matter is fully converted into components that are available in the environment while the pressure of the separate components equals the partial pressure of the respective component in the environment.

For the calculation of the exergy of an amount of matter it is required to select a system that will be able to bring the matter in full equilibrium with the environment. In order to derive useful equations it is necessary to divide the required conversion system in a number of sub-systems for which the produced work easily can be determined. Then the total work delivered by all sub-systems together equals the exergy of the amount of matter.

Dividing the conversion system in sub-systems is in particular necessary for the calculation of the exergy of mixtures. A first division is made here to distinguish between the thermo-mechanical exergy and the chemical exergy. Assuming that a gas mixture is available at a pressure and temperature that differ from the environmental conditions, the mixture will be brought at environmental conditions. An equation for calculating the work generated by performing this conversion with a suitable system is derived in section 3.3. The work from this conversion is called the thermo-mechanical exergy as it brings the mixture in thermo-mechanical equilibrium with the environment. During this conversion the composition of the gas mixture will remain unchanged. Next the mixture must be brought into full equilibrium with the environment by converting the mixture isothermally into environmental components at the partial pressure of the respective components in the environment. The work generated during this conversion is called the chemical exergy, because it is the maximum amount of work that can be derived by changing the chemical composition of the mixture keeping temperature and total pressure constant. Obviously all sub-systems together have to fulfil the characteristics as described in section 3.3. The exergy of the mixture equals the sum of the mechanical exergy and chemical exergy, thus:

$$Ex_{mixture} = Ex_{tm} + Ex_{ch} \tag{36}$$

In the following a procedure is presented for the calculation of the chemical exergy of gas mixtures. In this procedure the calculation of the exergy of a gas mixture occurs in two steps:
1. Determining the exergy of a gas mixture based on known exergy values for the respective elements at standard pressure and temperature;
2. Determination of the exergy of the elements based on a predefined environmental composition.

An overview of the necessary sub-systems for the first step is shown in figure 4. In order to convert a gas mixture into the respective elements the consisting components must be separated first; this occurs in system 2 of figure 4. Therefore it is supposed that the components can be isolated from the mixture by applying reversible membranes through which only one specific component can pass without friction while all other components are hold up. After passing the membrane a component is available at a pressure that equals its partial pressure in the mixture. Then this separation will occur without the need for any work. After separation the components have to be pressurised isothermal and reversibly till environmental pressure. Under these conditions it is assumed that components will fulfil the ideal gas laws. Then the work required for the compression can be calculated using the following equation:

$$W_{rev} = -\int_{1}^{0} V \cdot dp = -\int_{1}^{0} \frac{R \cdot T_0}{p} \cdot dp = -R \cdot T \cdot \int_{1}^{0} \frac{dp}{p} \tag{37}$$

Using this equation the work necessary for the separation of one mole of mixture (the work done by sub-system 2) becomes:

$$W_{rev,2} = \sum_i -y_i \cdot R_m \cdot T_0 \cdot \ln \frac{p_0}{y_i \cdot p_0} \tag{38}$$

In this equation y_i is the mole fraction of the respective components in the gas mixture.
In a second step, sub-system 3a, the isolated components are reversibly dissociated into their elements. The reactions necessary for this conversion are reverse formation reactions. As the work from a formation reaction equals the negative value of the change in the Gibbs-free energy, the work for the dissociation of one mole of a component becomes:

$$W_{rev} = \Delta_f g_{298}^{0,mol} \tag{39}$$

Then, for the work from the dissociation reactions to convert all components from one mole mixture it can be written:

$$W_{rev,3a} = \sum_i y_i \Delta_f g_{i,298}^{0,mol} \tag{40}$$

After sub-system 3a all compounds in the gas mixture are converted into their elements at standard pressure and temperature. As it is assumed that the exergy of these elements is known, the chemical exergy of the mixture can be calculated by adding up the different contributions:

$$ex_{mol,ch} = W_{rev,2} + W_{rev,3a} + \sum_i v_i \cdot ex_{mol,element} \tag{41}$$
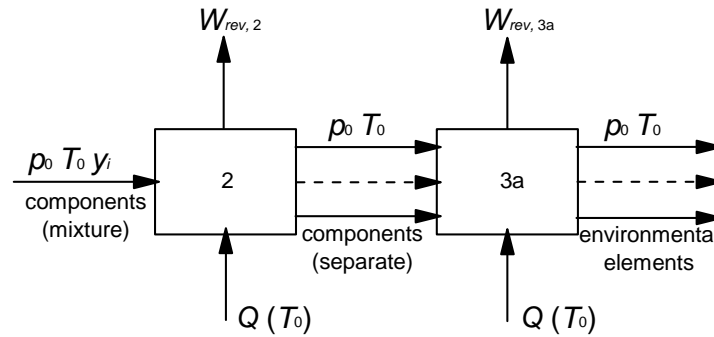

Figure 4 *Overview of sub-systems for the calculation of the exergy of a gas mixture, assuming that the exergy of available elements is known*

In equation 41 it is assumed that the molar exergy of the elements is known. The exergy values of the elements will be determined here in a second step. Therefore the element must be converted reversibly and isothermal into a compound or element that exists in the (defined) environment. In figure 5 the necessary sub-systems for the calculation of the exergy of an element are shown. For the conversion of elements into an environmental compound only matter from the environment can be used.
In order to bring an <u>element</u> in full equilibrium with the environment it must be converted first in an environmental component if the element does not exist as such in the environment. If for instance the surrounding air is used as the defined environment to determine exergy values, the elements carbon (C) and hydrogen (H_2) must be converted into CO and H_2O respectively by using oxygen from the environment. In case of elements like O_2 and N_2, which do exist as such in the environment, no conversion is necessary. The conversion of the element into an environmental compound occurs in sub-system 3b (see figure 1.5) and is actually the formation reaction of the environmental compound. The work from a formation reaction equals the negative value of the change in Gibbs-free energy.
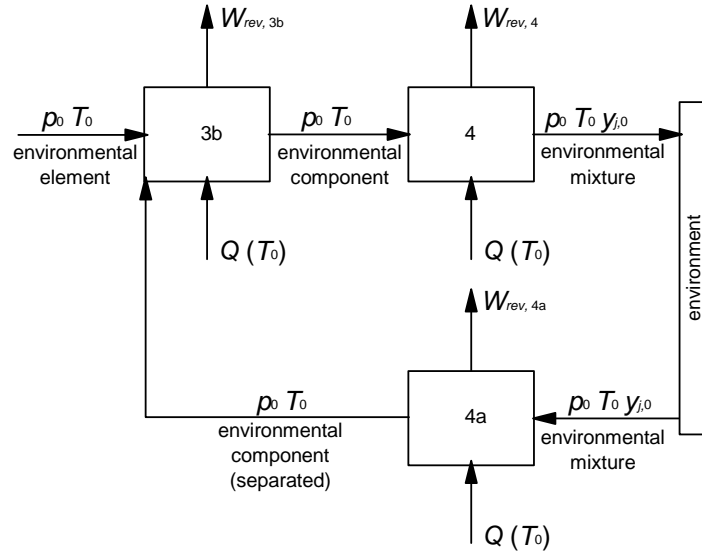
Figure 5 *Overview of sub-systems for the calculation of the exergy of elements*

As the formation reaction of one mole of compound requires ν mole of the considered element, the work from the conversion in sub-system 3b becomes:

$$W_{rev,3b} = -\frac{1}{\nu} \cdot \Delta_f g_{298}^{0,mol} \qquad (42)$$

As the conversion of 1 mole of the considered element requires ν_0 mole of an environmental component, this component has to be separated from the environmental mixture at its partial pressure and reversibly compressed till standard pressure. This extraction of the component is supposed to occur in sub-system 4a. The work from this sub-system, the work from compression is:

$$W_{rev,4a} = -\nu_0 \cdot R_m \cdot T_0 \cdot \ln \frac{y_j \cdot p_0}{p_0} \qquad (43)$$

In this equation y_j is the mole fraction of the respective component in the environment. The compound resulting from the formation reaction in sub-system 3b becomes available at standard pressure. The reversible discharge of this compound to the environment requires that it be expanded first to its partial pressure in the environment. After this expansion it is assumed to be discharged to the environment without pressure loss via a reversible membrane. The reversible work from the isothermal expansion becomes:

$$W_{rev,4} = -\frac{1}{\nu} \cdot R_m \cdot T_0 \cdot \ln \frac{p_0}{y_j \cdot p_0} \qquad (44)$$

The exergy of the element then equals the reversible work from the sub-systems necessary for the reversible conversion of the element into an environmental component, so:

$$ex_{mol,element} = W_{rev,3b} + W_{rev,4} + W_{rev,4a} \qquad (45)$$

With the equations (42) till (45) the chemical exergy of one mole element can be calculated, provided that a composition of the environment consisting of gaseous components is defined and that at least one of these components contains the considered element.
It must be noticed that some authors apply a further subdivision of the chemical exergy into chemical exergy and mixing exergy. Here the chemical exergy includes the chemical exergy as well as the mixing exergy. Dividing these terms has only limited advantages, but can result in serious confusion with regard to the accurate definition of the mixing exergy.